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Fluorine in the environment, a review of its sources and geochemistry

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Abstract

While F is an essential constituent of some rock-forming minerals such as fluorite and apatite, its major occurrence in the lithosphere is within hydroxysilicate minerals where F⁻ occupies OH⁻ lattice sites. The majority of the F occurring in the secondary environment derives from natural weathering processes with some soils derived from F-rich parent rocks containing over 1 weight (wt) % F. Other natural sources of F are vulcanicity, wind-blown dust and a minor marine-derived component, with biomass burning, being in part natural, also a source. Several anthropogenic sources of environmental F have also been identified. Of the anthropogenic sources, the application of phosphate fertiliser, which probably adds over 2.3 Mt a⁻¹ F to soils globally, represents the largest. While much of this is strongly retained in soils, some may be transferred to groundwater. In some abandoned mine sites in the UK where fluorite was associated with the mineralisation, soil F contents of up to 8 wt % have been recorded with plants growing on the sites containing up to 1 wt % F.

The rapid growth of urban areas in India, Pakistan and Bangladesh has resulted in an upsurge of brickmaking in Asia, with these 3 countries plus China accounting for over 75% of global brick production. As a result there is a large number of unregulated brick kilns which emit HF into the surrounding environment. Based on an annual global brick production of 1,500 billion and the F contents of brick clays, it is estimated that about 1.8 Mt a⁻¹ F are released to the environment from brick manufacture. This suggests that brickmaking is the largest source of atmospheric F emissions dwarfing that of coal combustion, 0.2 – 0.3 Mt a⁻¹, phosphate fertiliser production, 0.07 – 0.10 Mt a⁻¹, aluminium smelting, 0.041 Mt a⁻¹, and even vulcanicity, 0.3 – 0.7 Mt a⁻¹. However, it is apparent that atmospheric F emissions are not transported globally and as such their effects are manifested only in the local environment. Emissions from industry sited close to urban centres can impact these environments together with domestic coal combustion and the release of F from high octane fuels in motor vehicles.

A more recent source of F in the environment stems from the large number of fluorocarbon compounds in everyday use. Degradation of some of these fluorocarbon compounds together with pyrolysis of fluoropolymers and burning of household refuse has resulted in the deposition of organofluorine compounds such as trifluoroacetic acid in the environment.

1. Introduction

Fluorine is ubiquitous in the environment with most deriving from natural sources, these being: normal weathering processes resulting in F release from rocks and minerals, volcanic activity and marine aerosol emission, together with biomass burning, being in part natural. However, there are several sources of anthropogenically-derived F which in some areas represent a threat to the biosphere. Anthropogenic sources can be broadly subdivided into

those deriving from industrial processes, which include coal fired power generation, brick making and ceramic manufacture, aluminium production and phosphate fertiliser production, and those deriving from agricultural practices such as phosphate fertiliser and sewage sludge application, and the use of F-containing herbicides and pesticides etc.

It has been suggested that F is an essential element for humans and other animals (Underwood, 1977; Adriano, 1986) but this has not been proven unequivocally (Fordyce, 2011). However, it is well known that in low concentrations fluorine, in the form of F^- , is beneficial to human health. The early work of Dean (1938) and his co-workers (Dean et al., 1941, 1942) showed that small quantities of ingested F^- promote the development of healthy teeth and help to protect them from caries. It has also been suggested that dietary F^- promotes strong bone formation (Jha et al., 2011) and possibly aids the prevention of osteoporosis (Ozsvath, 2009). However, while ingestion of relatively small quantities of F^- have a beneficial effect on teeth and bone, ingestion of elevated concentrations of F^- has a harmful effect, causing dental and skeletal fluorosis (Fewtrell et al., 2006). Dental fluorosis has been estimated to affect in excess of 70 million people globally with at least 2.7 million people in China and India alone suffering from skeletal fluorosis (Fawell et al., 2006), while some workers suggest that the numbers affected by fluorosis globally are as high as 200 million (Ayoob and Gupta, 2006). UNICEF (2016) lists 27 countries where fluorosis is endemic.

The major pathway of F into the body, as F^- , is via drinking water and Dissanayake (1991) suggests that concentrations of $0.5 - 1.5 \text{ mg L}^{-1}$ will promote healthy teeth, with concentrations in excess of 1.5 mg L^{-1} causing dental fluorosis and concentrations in excess of 4 mg L^{-1} resulting in skeletal fluorosis. The World Health Organization (WHO, 2017) suggests a guideline value of 1.5 mg L^{-1} in drinking water. However, it is apparent that there are modifying influences such as the amount of water consumed on a daily basis, which generally reflects climate, *e.g.* in Ghana it has been shown that dental fluorosis occurs in areas where the concentration in the water is 1.5 mg L^{-1} (Craig et al., 2015). The major problems with regard to human fluorosis are manifested in areas where the domestic water supply derives from F-rich groundwaters. In the majority of cases, the source of F in these waters is natural. The global distribution of F-rich waters has been reviewed by Edmunds and Smedley (2013) and Ali et al. (2016).

In some cases F-rich foods can contribute to the overall body load (Ozsvath, 2009) with the tea plant, in particular, being a natural concentrator of F (Fordyce, 2011) with dental and even skeletal fluorosis having been shown to result from drinking tea (Fung et al., 1999; Kakumanu and Rao, 2013). Other modifying effects are the diets of affected populations, with low-protein diets exacerbating the problem (Fordyce, 2011), in addition, it has been demonstrated that low calcium and Vitamin D intakes are associated with increased fluorosis (Patel et al., 2017). It has also been shown that domestic animals can suffer from fluorosis due to consumption of high- F^- waters (Choubisa, 2012).

Dental and skeletal fluorosis are the major problems resulting from F intoxication, however, other adverse health outcomes have been postulated. These outcomes include cancer of various organs, low IQs in children, renal problems and interference with endocrine systems amongst others (Ozsvath, 2009). However, there is limited proof of these outcomes and

research is ongoing. A detailed account of the health problems associated with F⁻ intake is beyond the scope of this review and the reader is referred to reviews by Ozvath (2009) and Fordyce (2011) for a broader discussion of the topic.

The aim of this review is to discuss and assess the relative importance of the various natural and anthropogenic sources of environmental F.

2. Fluorine geochemistry

2.1. Lithogeochemistry

Fluorine is the lightest of the halogen group and is the most electronegative element. As such it is highly reactive and it is widely stated in the literature that elemental fluorine does not exist naturally in the free state but, recently, Schmedt auf der Günne et al. (2012) have demonstrated the presence of F₂ in a radioactive variety of fluorite, antozonite, using NMR spectroscopy. However, F normally exists in nature as the F⁻ ion.

Fluorine is a lithophile element (Levinson, 1980) being concentrated in the crust of the Earth (Hanley and Koga, 2018). Rudnick and Gao (2014) indicate that relatively few attempts have been made to estimate the F content of the upper continental crust but suggest a figure of 557 mg kg⁻¹, derived from the average of previous estimates. These authors suggest that the bulk continental crust contains 553 mg kg⁻¹. Earlier estimates such as those of Wedepohl (1995) suggest that the F content of the bulk crust (525 mg kg⁻¹) is somewhat different to that of the upper continental crust (611 mg kg⁻¹), due to the element's lithophile behaviour.

Of the rock-forming minerals in which F is an essential constituent only fluorite (CaF₂) and, to a lesser extent, topaz (Al₂SiO₄(F,OH)₂) are relatively common (Koritnig, 1972), while cryolite (Na₃AlF₆) and bastnäsite ((Ce, La, Nd)CO₃F) can occur in some granitic pegmatites (Bailey, 1977), and villaumite (NaF) can occur in some peralkaline, nepheline-containing igneous rocks (Stormer and Carmichael, 1970) and has also been identified in evaporate minerals in Lake Magadi, Kenya (Nielsen, 1999). Several other minerals which contain F as an essential component have been identified in pegmatitic rocks and in metasomatically/hydrothermally altered rocks (Koritnig, 1972).

In most rocks these F-containing minerals account for a relatively small percentage of the total F content. The major control on the lithogeochemistry of F is the similarity of the F⁻ and the OH⁻ ions with ionic radii of 131 pm and 135 pm, respectively (Li et al., 2017). Due to this similarity the F⁻ ion easily substitutes for the OH⁻ ion in rock-forming minerals. It is, therefore, not surprising that hydroxyl-containing silicates and apatite are the major hosts of F in the lithosphere.

A summary of concentrations in the major rock types is included in Table 1. According to Koga and Rose-Koga (2018) in the rocks which make up the continental crust F predominantly ranges up to 900 mg/kg, being fairly evenly distributed within the major rock types. However, within the different rock types there are wide variations in F content. In general, the F content of igneous rocks increases with silica content being highest in felsic and lowest in ultramafic rocks. Fluorine is considered to be an incompatible element in that

during crystallisation of a melt it does not enter early forming minerals so becoming strongly concentrated in the late stage melt and is enriched in the final differentiates (Stormer and Carmichael, 1971; Fuge, 1977). Thus granitic pegmatites can contain concentrations of over 1wt % F. Fluorine also becomes concentrated in the late stage hydrous fluids which can lead to hydrothermal and metasomatic alteration of the granites resulting in extreme F enrichment (Table 2). In addition, alkalic and silica undersaturated igneous rocks are also generally F-rich, with some carbonatites containing up to 2.5wt % F. (Table 2).

Of the common sedimentary rocks only shales are relatively enriched in F, ranging up to about 800 mg kg⁻¹, with sandstones and carbonates generally containing <300 mg kg⁻¹ (Table 1). However, sedimentary phosphorites are strongly enriched in F with concentrations in the region of 4 wt % (Table 2).

2.2. Soil geochemistry and plant uptake

The fluorine content of most soils ranges between <10 and 1000 mg kg⁻¹, however, values in excess of 1wt % have been recorded in uncontaminated soil (Table 3). The F content of soils reflects that of the parent material, for example, high F soils occurring over F-rich granites (Table 3). However, retention of F in a soil generally reflects its clay content as clay minerals strongly adsorb F⁻ (Weinstein and Davison, 2004) with the greatest adsorption occurring in slightly acidic soils (Liu et al., 2014). As a result clay-rich soils tend to be rich in F (Weinstein and Davison, 2004). In addition to the adsorption of F by clays in soil, according to Liu et al. (2014), F⁻ replaces OH⁻ in the clay minerals.

Davison and Weinstein (2006) state that soils are a source of F for the biosphere but also act as a sink for atmospherically deposited F. They further suggest that F added to the soil from the atmosphere tends to be leached down the profile, resulting in surface soils being generally lower in F than deeper soil horizons. However, the strong ability of clay minerals to adsorb F⁻ causes it be retained in the sub-surface horizons. Aluminium and Fe oxyhydroxides are also strong adsorbents of F⁻ in soil and aid in the immobilisation of atmospherically deposited F (Cronin et al., 2000). The ability of soils to retain F is well illustrated by the case of Mt. Etna volcano, Italy, where large quantities of F-rich gases are evolved continuously. The groundwaters in the aquifers occurring on the flanks of the volcano, which are important sources of potable water, have been protected due to the retention of F by the soils (D'Alessandro et al., 2012).

The bioavailability of soil F is generally low, particularly in soils with a pH of 5.5 – 6.5, so that little soil F is incorporated in plants (Weinstein and Davison, 2004). In addition, soil-derived F is prevented from being incorporated into the aerial parts of plants through exclusion by the roots (Davison and Weinstein, 2006). However, it is generally accepted that where there is a source of atmospheric F it is incorporated in plants by uptake through the leaves, with direct aerial uptake being the dominant pathway (Davison and Weinstein, 2006). According to Weinstein (1977) F⁻ is the most phytotoxic air pollutant.

2.3. Fluorine in waters

Unpolluted surface waters are generally low in F^- with De Vos et al. (2006) quoting values ranging from $<0.05 - 1.6 \text{ mg L}^{-1}$ with a median of 0.1 mg L^{-1} for stream waters analysed for the FOREGS Geochemical Atlas of Europe. The highest values generally reflect geological influences such as F-rich granites, recent volcanics or fluorite mineralisation, with some reflecting input of F-rich groundwater. Surface waters impacted by F-rich hydrothermal waters can be strongly enriched, with values of up to 2800 mg L^{-1} quoted by Ali et al. (2016).

Groundwaters can become strongly concentrated in F^- with some values for global groundwaters quoted by Ali et al. (2016) ranging up to over 20 mg L^{-1} . The F content of waters is controlled by fluorite solubility and hence the Ca content of the water (Edmunds and Smedley, 2013). In general, F-rich groundwaters fall into the following categories (Edmunds and Smedley, 2013; Ali et al., 2016):-

- i) Those occurring in arid/semiarid areas where there has been evapoconcentration resulting in Na-rich/Ca-poor waters
- ii) Old groundwaters – where there has been water-rock interaction with Ca-Na exchange resulting in low Ca waters
- iii) Those occurring in crystalline basement rocks
- iv) Those occurring in areas of alkalic igneous rocks (*e.g.* Great Rift Valley, East Africa)

As stated earlier, F-rich groundwaters used as potable water sources have resulted in serious fluorosis in many countries. The global occurrence of these waters is reviewed by Edmunds and Smedley (2013) and Ali et al. (2016).

3. Uses of fluorine

Fluorite or fluorspar (CaF_2), derived from hydrothermal deposits, is the only mineral mined as a commercial source of F (Hayes et al., 2017), with 6 Mt extracted globally in 2017, the bulk of this extraction being in China (63%) and Mexico (26%) (U.S. Geological Survey, 2018). A relatively minor source is also afforded by fluorosilicic acid (H_2SiF_6), which is a by-product of the manufacture of phosphate fertiliser, via phosphoric acid, from F-containing apatite. Fluorine has a wide range of uses in industry and manufacturing. Fluorite itself is used in the steel industry as a flux, improving the fluidity of the melt. It is also used in the ceramics industry, glassmaking and manufacture of fibreglass, and in coatings on welding rods (U.S. Geological Survey, 2018).

The major use of fluorite is, however, in the production of HF which is then used in the production of fluorine gas and in the manufacture of the very many F-containing chemicals and materials in use globally (Harsanyi and Sandford, 2015). The major uses of HF, as listed by Villalba et al. (2007), are the production of fluorocarbons and the manufacture of synthetic cryolite and AlF_3 , for use in the Hall-Héroult process for the isolation of Al metal from Al_2O_3 , however, Kvande (2011) suggests that in modern systems, relatively small quantities of cryolite are used up in this process.

The C – F bond is extremely strong and difficult to rupture, hence, fluorocarbon compounds are very stable (Key et al., 1997). Organofluorine compounds have found use in a large

variety of everyday human activities. Many fluoropolymers are manufactured and have a wide range of uses, being very stable, non-corrosive and resistant to heat, they are used extensively in industry, for example, as lubricants which can withstand high temperatures, wire insulation materials and in vacuum pumps (Villalba et al., 2007). In addition, fluoropolymers are used for waterproof roofing materials and waterproof clothing and as non-stick surfaces on cookware in addition to many other uses (Harsanyi and Sandford, 2015).

Fluorine is incorporated into a large variety of compounds that are used in medicine and agriculture. The incorporation of F in pharmaceuticals has been found to improve their biological reactivity and to enhance their bioavailability (Böhm et al., 2004; Maienfisch and Hall, 2004). Prior to the 1970s F-containing medicines were rarely used (Böhm et al., 2004), however, according to Wang et al. (2014) there are about 200 pharmaceuticals now in use which contain F and, according to Harsanyi and Sandford (2015), 20% of all new pharmaceuticals entering use daily are F-containing. In addition, the major anaesthetics in use currently are fluorinated gases (Harsanyi and Sandford, 2015). Fluorine is also incorporated into many agrochemicals with Tomoya and O'Hagan (2014) suggesting that about 25% of herbicides currently in use contain F. According to Jescke (2010) the use of F-containing agrochemicals has shown a steady increase since the 1950s with major expansion in their use from the 1980s. These F-containing compounds are used as insecticides, fungicides, herbicides, acaricides and nematicides (Jescke, 2010) with many continuing to be developed (Jescke, 2017).

Hydrofluoric acid is also used for etching glass and in the manufacture of semiconductors for the microelectronics industry. It is also used in oil refineries as an alkylation catalyst to obtain high-octane fuels. Villalba et al. (2007) also note the use of HF for the enrichment of uranium by converting it to UF_4 and, subsequently, UF_6 . Sulfur hexafluoride is another important compound manufactured from F and, due to its inertness, has many uses in the electrical industry, in particular, but also finds use in the medical field and as a general tracer gas. Fluorine is incorporated into toothpaste and mouthwashes to help prevent tooth decay and in some countries and regions is added to water supplies to aid dental health.

4. Natural sources of fluorine in the environment

4.1. Volcanicity

Fluorine is released from volcanoes predominantly as HF gas (Symonds et al., 1988) with minor amounts emitted in other gases such as Si-containing compounds (D'Alessandro, 2006). Gaseous HF interacts with and is adsorbed onto the surface of volcanic ash (Óskarsson, 1980) and during eruptions the majority of F release is by way of ash (Bellomo et al., 2007). However, over 90% of F release occurs during quiescent degassing (Symonds et al., 1988) and during this phase it is released as HF (Bellomo et al., 2007). Francis et al. (1998) found that during quiescent degassing of Mount Etna, Sicily, Italy, 190 t of HF are released daily, which amounts to an annual release of almost 70,000 t, making it the largest point source of atmospheric F emissions on Earth.

While F-rich gases impact the whole environment in volcanic regions, the major concern regarding volcanogenic F is its impact on drinking waters and the deposition of F-containing ash on plants and soils in the vicinity of the eruption, the major pathway into the biosphere being via impacted waters and crops etc (D'Alessandro, 2006; Ranjan and Ranjan, 2015). Fluorine in volcanic ash is solubilised in the digestive systems of grazing animals (Cronin et al., 2003) and there are many examples of grazing animals developing chronic fluorosis as a result of ingestion of F-rich ash with both domestic and wild animals being affected (Cronin et al., 2003; Weinstein et al., 2013; Ranjan and Ranjan, 2015). Severe dental fluorosis has been recorded in juvenile red deer following an eruption of the Puyehue–Cordon Caulle volcano, Argentina, in 2011 (Flueck and Smith-Flueck, 2013). Major problems of fluorosis in livestock have been recorded in Iceland where magmas are F-rich (D'Alessandro, 2006). The first description of fluorosis in sheep was given after the 1693 eruption of Hekla (Fridriksson, 1983), while the Laki eruption in 1783-84 resulted in catastrophic loss of life for both humans and domestic animals due to the impact of the estimated 7 Mt of HF released (Williams-Jones and Rymer, 2015). In addition to causing fluorosis in grazing animals, the extreme phytotoxicity of HF caused crops to perish, so resulting in starvation of animals and humans, the major reason for the catastrophic loss of life after the Laki eruption (Weinstein et al., 2013). Flueck (2016) reports that ruminants are particularly prone to fluorosis from ingested volcanic ash with fluorosis in grazing animals in Patagonia being manifested some months after the deposition of the ash.

Volcanic activity has resulted in F⁻ enrichment of surface and groundwaters in many countries (Stewart et al., 2006; Flaathen and Gislason, 2007). Impacts on water can be from dissolution of HF gas but for the most part F enrichment in water is due to its interaction with ash, with ash leachate studies suggesting that concentrations of soluble F⁻ range up to several thousand mg L⁻¹ (Witham et al., 2005). Gislason et al. (2011) found that ash from the 2010 eruption of the Eyjafjallajökull volcano, Iceland, had 6.9% F in its surface coating and that 16% of this was soluble in pure water. The major pathway into humans is through drinking waters (D'Alessandro, 2006) with Baxter et al. (1999) recording dental fluorosis in populations of villages on São Miguel Island, in the Azores, due to drinking spring water from the caldera of the Furness volcano. In Goma, Democratic Republic of the Congo, rainwater is a major source of potable water and, due to its interaction with a plume deriving from the Nyiragongo and Nyamulagira volcanoes, is enriched in F⁻ which has resulted in dental fluorosis in the population (Balagizi et al., 2017).

Volcanic emissions have been suggested to be the major source of F to the atmosphere (Friend, 1989; Tavener and Clark, 2006). Some attempts have been made to estimate the annual global total of HF release from volcanoes. The most commonly quoted values in the literature are those of Symonds et al. (1988) who suggested a value of 0.06 – 6 Mt and Halmer et al. (2002) who derived a value of 0.7 – 8.6 Mt. However, more recently, Pyle and Mather (2009) have been critical of previous estimates for this global flux on the basis of the methods used for the estimation. These authors further quote an estimate of 0.5 ± 0.2 Mt for the annual global flux of arc-related volcanoes, which they suggest dominate the global volcanic efflux. While F emissions from mid-ocean ridges and intraplate volcanics are also

likely to produce significant quantities of HF, it seems probable that global atmospheric emissions from volcanoes may not be as great as previously thought.

4.2. Marine-derived fluorine

It has been proposed that marine aerosols and spray make a very significant contribution to atmospheric F and to its geochemical cycle (Friend, 1989; Taverner and Clark, 2006). Friend (1989) suggested that the annual marine flux of F, supposed to be 0.4 to 1 Mt, to the atmosphere is second only to the volcanic flux, while Taverner and Clark (2006) quote values of between 1 and 2 Mt. However, other authors (*e.g.* Cadle, 1980; Lewandowska et al., 2013) suggest the lower value of 20,000 t for this flux.

The mean F content of seawater is 1.3 mg L^{-1} (Carpenter, 1969) and it has been suggested that marine-derived F is an important component in the hydrogeochemical cycle of F. Sugawara (1967) quoted data for samples of Japanese precipitation that imply that F^- is strongly enriched relative to Cl^- and that the major source is seawater, while Carpenter (1969) also states that most F in global precipitation derives from the sea. It has been suggested that F is emitted from seawater in gaseous and particulate forms, the gaseous component being HF (Friend, 1989; Taverner and Clark, 2006). According to Carpenter (1969), relative to Cl^- , F is preferentially enriched in marine emanations to the atmosphere with the F/Cl ratio of precipitation being 10-1000 times that of seawater. Neal et al. (1990) in a study of rainfall in mid Wales, UK, also suggested that there is some enrichment of F relative to Cl.

However, Wilkniss and Bressan (1971) demonstrated that, in general, there was no preferential enrichment of F^- in marine-derived aerosols; these authors also found that where F^- concentrations were elevated in aerosols it was due to a high dust content. This was confirmed by Barnard and Nordstrom (1982) who found no significant difference between the F^- content of pristine coastal and inland rainfall samples collected in the USA. There was no correlation with Na concentrations (as a proxy for sea salt), which was interpreted as indicating no enrichment from the sea. It was also concluded that the major source of F^- in rainwater was anthropogenic. Saether et al. (1995) in a study of F^- in precipitation in southern Norway also concluded that there was no preferential enrichment from the sea surface with their data suggesting that, in general, less than 1.5% of F^- in precipitation derives from the sea, with the majority deriving from anthropogenic sources. In addition, De Angelis and Legrand (1994) in a study of F^- in ice and firn from Greenland found that there was an insignificant sea-salt particle contribution.

However, some authors have suggested that coastal rainfall is enriched in F^- , with Linder and Frysinger (2007) reporting that rainfall from within 10 km of the coast of South Carolina had a mean F^- content of 0.17 mg L^{-1} compared with 0.06 mg L^{-1} between 40 and 50 km from the coast. Lewandowska et al. (2013) found F^- to be enriched in marine-derived PM_{10} aerosols over a coastal site in Gdynia, Poland when airspeeds increased to over 10 m sec^{-1} , the F^- content correlating significantly with the Na content. It has also been reported that in some coastal areas of mid Wales, UK, stream water and runoff are relatively enriched in F^- reflecting a marine input (Neal, 1989; Neal et al., 1990; BGS, 1999). In addition, Mikkonen

et al. (2018) have demonstrated that coastal soils in Victoria, Australia are enriched in F⁻ relative to those from inland areas with F⁻ content correlating with Na⁺ content.

Despite the conflicting evidence it seems likely that the contribution of marine-derived F to the atmosphere has been over estimated and is fairly insignificant when compared to the volcanic and anthropogenic fluxes. While marine derived F may well influence the chemistry of coastal rainfall, runoff and soil, it seems likely that its influence only extends about 10-20 km inland.

4. 3. Wind-blown dust

Weinstein (1977) suggested that wind-blown soil could make a significant contribution to atmospheric F content. On the basis that in the USA alone about 30 Mt of soil are removed annually by wind action, this would add about 6,000 t of F to the atmosphere. Analytical data on ice cores from Greenland (De Angelis and Legrand, 1994) and the French and Swiss Alps (Preunkert and Legrand, 2001) suggest that wind-blown dust, deriving from soils, constitutes a significant source of F⁻ in precipitation. Indeed, Preunkert and Legrand (2001) state that prior to 1930 wind-blown dust was the dominant source of atmospherically deposited F⁻. While the source of F⁻ through the 1930s to 1980 was predominantly anthropogenic, Preunkert and Legrand (2001) found that from 1980 to 2000 wind-blown dust accounted for $18 \pm 2\%$ of the F⁻ in ice cores from the Alps.

4.4. Biomass burning

Biomass burning can result from natural processes and from human actions, with the latter being both intentional, as in the agricultural practice of stubble burning, and from accidental fires (Yadav and Devi, 2018). While the great majority of biomass fires are anthropogenically sourced, natural fires tend to destroy larger areas of vegetation than human induced fires (Yadav and Devi, 2018). For this reason, the author has included biomass burning under the general heading of natural processes.

Several authors have commented on the potential contribution of biomass burning to atmospheric releases of fluorine (e.g. Weinstein and Davison, 2004). De Angelis and Legrand (1994) found elevated F concentrations deriving from biomass burning, in high latitudes, in the Greenland ice cap, while Lewandowska et al. (2013) report biomass burning as a source of F in PM₁₀ aerosols in the Baltic Sea area of Poland. More recently Jayarathne et al. (2014) have attempted to determine the degree of F emission from biomass burning experimentally. Different biomass types were subjected to combustion in the laboratory and the degree of F emission was determined. On the basis of the results, Jayarathne et al. (2014) suggest that biomass burning releases significant amounts of fine particulates (PM_{2.5}) containing F. The degree of F release varied with plant type and with geographic distribution.

Jayarathne et al. (2014) estimate that 76,000 t of F are released annually from biomass burning, which they suggest is comparable to that released from coal combustion.

5. Industrial sources of fluorine in the environment

5.1. Coal combustion

Coal combustion has been suggested to be one of the major sources of anthropogenic F (Weinstein and Davison, 2004), while F has been listed as one of the most hazardous elements emitted during coal combustion (Yang et al., 2017). The world average for the F content of coal has been calculated to be 88 mg kg^{-1} (Ketris and Yudovich, 2009) and a high percentage of this is released during combustion. Chen et al (2013) suggested that almost 80% of the F in coal is released to the atmosphere at 800°C , this being in gaseous and particulate forms (Doley et al., 2004), with Yu et al. (2004) demonstrating that 100% of the F in coal is released at $1100\text{-}1200^\circ\text{C}$.

Several studies have shown that F release during coal combustion has resulted in environmental pollution, damage to plants and fluorosis in animals and humans. Doley et al. (2004) state that emissions from coal-fired power stations represent the largest individual source of atmospheric F in Australia with impacts on plants being recorded. Burns and Allcroft (1964) recorded fluorosis in grazing animals in the vicinity of coal-fired power stations in the UK. Fidanci and Sel (2001) reported that F emissions from the Yatağan coal-fired power station in Muğla Province, SW Turkey, have resulted in chronic fluorosis in sheep. Studies in Europe have shown that fluorosis occurs in wild animals as a result of emissions from coal-fired power stations such as in the NW of the Czech Republic (Zemek et al., 2006; Kierdorf et al., 2012).

However, it is in China that the worst problems associated with F release from coal combustion have been manifested as it is a major producer of coal and consumes about half of the global total production (BP, 2018; Finkelman and Tian, 2018), it being the country's major energy resource (Chen et al., 2013; Yang et al., 2017). Chinese coals contain an average of 130 mg kg^{-1} F (Dai et al., 2012) with coals from some regions of southern China such as Guizhou Province having been found to contain as much as 3575 mg kg^{-1} (Dai et al., 2015). Chen et al. (2013) claimed that F emissions from coal combustion increased steadily through 2005 to 2009, estimating that in 2009, over 162,000 t F were emitted.

Human fluorosis due to F release from the combustion of coal indoors has only ever been reported from China (Dai et al., 2012). Dental and skeletal fluorosis due to coal combustion have been reported in several Chinese provinces (Ando et al., 1998; Finkelman et al., 1999), with over 18 million people affected in 2000 (Li et al., 2003). It is likely that much of the exposure to F derives from the burning of coal in open stoves and utilisation of the stoves to dry and preserve foodstuffs, such as corn and chillies (Ando et al., 1998; Zheng et al., 1999; Finkelman et al., 2002) with some also deriving from direct inhalation (Ando et al., 1998; Dai et al., 2012). Dai et al. (2007) recorded F contents of corn and chillies dried over open fires as 1419 mg kg^{-1} and 110 mg kg^{-1} , respectively. While it has been suggested that the source of F is directly due to its release from coal (Li et al., 2003; Liu et al., 2007), some authors have implicated the use of F-rich clay, used to bind the coal into briquettes, as a major source of F release during combustion (e.g. Wu et al., 2004; Dai et al., 2007). Dai et al. (2007) in a study

of fluorosis in Zhijin County, Guizhou Province, quote mean values for F of 237 mg kg⁻¹ in coal, 2262 mg kg⁻¹ in the clay binder and 828 mg kg⁻¹ in the coal/clay mixture.

Hong et al. (2017) have highlighted F emissions related to subsurface coal seam fires and determined F in soils and plants in the vicinity of such a fire in Inner Mongolia, which has been burning for over 50 years. Fluorine contents of up to 1670 mg kg⁻¹, with a mean of 1250 mg kg⁻¹, were recorded for soils in the vicinity of the fire, compared to a background of 240 mg kg⁻¹. Plant leaf samples in the vicinity of the fire showed a mean value of 523 mg kg⁻¹ with a background of 76 mg kg⁻¹. In addition, an urban area in the vicinity was impacted with soils having F contents of 552 mg kg⁻¹. Coal seam fires are natural phenomena that occur in many countries (Finkelman, 2004) and as such could be serious sources of F contamination on a local basis.

In addition to the problems caused by coal combustion, it has been shown that coal waste can also be a source of environmental F contamination. Gao et al. (2016) determined F in coal waste in China to range up to 1885 mg kg⁻¹ with the mean content being 525 mg kg⁻¹. Soils in the vicinity of the waste tips contain 320-860 mg kg⁻¹ F compared to 180-550 mg kg⁻¹ in background soils. The authors further suggest that spontaneous combustion of coal spoil heaps releases 90% of the contained F which makes a significant addition to atmospheric F pollution, which could account for 40% of atmospheric F emissions in China.

While the majority of the F occurring in coal is lost to the atmosphere during combustion, some is retained in fly ash collected in electrostatic precipitators. Figures for the F content of fly ash generally suggest relatively low concentrations, with Tsubouchi et al. (2011) quoting values for Japanese fly ash ranging from 20-130 mg kg⁻¹ and Deng et al. (2016) values of 84-326 in ash deriving from various Chinese coals, while Córdoba et al. (2012) suggest a value of 123 mg kg⁻¹ for fly ash from a Spanish power plant. However, Ramya et al. (2013) quote a value of 2,024 mg kg⁻¹ for fly ash from two power stations, near Nagpur, central India. As fly ash is frequently disposed of in lagoons there is some concern that groundwaters may be impacted but Ramya et al. (2013) found that there is only moderate contamination of groundwater, ranging up to 3.1 mg L⁻¹ with most below 1.5 mg L⁻¹.

Coal combustion has been suggested to be the major anthropogenic flux of F to the atmosphere (Taverner and Clark, 2006), the annual flux having been estimated to be between 12,000 and 102,000 t (Jayarathne et al., 2014). However, as noted above, Chen et al. (2013) calculated that F emissions from coal combustion in China in 2009, were over 162,000 t. With China being responsible for utilising about 51% of the global coal output (BP, 2018), it seems likely that total global F emissions from coal combustion are in the range of 200,000 – 300,000 t, which is 2-3x higher than previous estimates.

5.2. Brickmaking

The manufacture of bricks has long been recognised as a source of environmental F contamination (*e.g.* Ost, 1907; Oelschläger, 1965). Bricks, along with tiles and drainage pipes, are made from clays and clay-rich rocks and the process involves roasting at temperatures of 900 – 1200 °C with temperatures of 1000 °C or more being favoured.

Fluorine is housed in the OH-containing minerals, such as the clays and micas etc., and most of this is evolved, mainly as HF and SiF₄, during the high temperature roasting (Troll and Farzaneh, 1978; Weinstein and Davison, 2004). Bonvicini et al. (2006) suggest that 57-82% of the F in brick clays is lost during firing at 1000 °C, while Xie et al. (2003) found that during roasting of soils used for brickmaking in southern China, the amount of F emitted increased from 57.2% to 85.4% between 700 and 1100 °C. In a study of variously sourced brick clays from the UK, Fuge and Hennah (1989) demonstrated that, in general, over 80% of F occurring in the brickmaking rocks was lost during roasting at 1000 °C (Table 4).

In the developed world the brickmaking industry, along with other industries with potential to emit F, has been heavily regulated and F emissions have been greatly reduced (Cape et al., 2003). However, there is still a problem with F release during brick making in the developing world where large quantities of bricks are manufactured to facilitate the rapid growth of urban areas, to the extent that Khalid et al. (2017) describe brick making as the fastest growing industry in southern Asia. In 2010, 1,500 billion bricks were produced globally with China, India, Pakistan and Bangladesh producing over 75% of them (Baum, 2010). While brick production in China is being modernised and becoming less of a pollution source, much of the brickmaking in the rest of the developing world is artisanal and heavily polluting (Schmidt, 2013). Many of the brickmaking facilities, which are in close proximity to urban areas, are poorly regulated and are serious sources of F emission (Ahmed et al., 2012). For example, Ahmed et al. (2012) state that in the urban and peri-urban area of the large city of Peshawar, Pakistan, there are some 400-450 brick kilns, with each producing some 800,000 bricks per month. Fluorine emissions from these kilns have been shown to cause foliar damage to fruit trees in the region and to reduce crop yields of bean and maize significantly (Ahmed et al., 2012, 2014). Many of the kilns use low quality coal along with waste oil and rubber tyres to fire the kilns (Jha et al., 2008; Khalid and Mansab, 2015). Rajarathnam et al. (2014) estimate that 25 Mt of coal are used in brick kilns in India annually. It is, therefore, likely that in addition to F released from clays during firing of the bricks, some is also released from the fuels.

On the basis that the manufacture of 1000 bricks requires approximately 3 t of clay (BGS, 2007), the 1,500 billion bricks being produced annually would require 4.5 billion tonnes of clay. Clays and clay-rich rocks used for brickmaking would generally be expected to contain 450 - 800 mg kg⁻¹ F (Koritnig, 1972; Xie et al., 2003) of which about 80% would be expected to be lost during firing (Fuge and Hennah, 1989; Xie et al., 2003). Assuming a mean F content of 500 mg kg⁻¹, suggests that in the region of 1.8 Mt F is released from roasting of brick clays annually. Notwithstanding that in many countries clean technology has been introduced into the brickmaking industry, it is apparent that the industry represents the major anthropogenic flux of F to the atmosphere, dwarfing that of coal.

The ceramic industry is also based on baking of clays to make tiles etc and, consequently, suffers from the same problems as the brick-making industry. Bonvicini et al. (2006) state that F emission during the production of ceramic tiles in the Sassuolo District, Modena and Reggio Emilia provinces, Italy is 727 t a⁻¹ of which they estimate 73 t a⁻¹ is emitted to the atmosphere. According to Bonvicini et al. (2006), the Sassuolo District produces about a 1/4 of

the global output ceramic tiles. On this basis the global F release from ceramic tile production is estimated to be about 290 t a⁻¹. However, no figures are available to enable estimation of F release from the manufacture of other ceramic items such as sanitary ware.

5.3. Aluminium smelting

Aluminium metal is produced from aluminium oxide by the Hall-Héroult process, whereby the Al₂O₃ is dissolved in molten cryolite (Na₃AlF₆), with some added AlF₃, and is subjected to electrolysis at 960 °C. During the electrolytic process F is released into the atmosphere in both gaseous and particulate forms, the gaseous releases are almost entirely HF but minor quantities of other F-containing gases such as CF₄ and C₂F₆ are also produced (Tjahyono et al., 2011; Kvande, 2014). The particulate species are Na and Al fluorides and cryolite (World Aluminium, 2018).

In the late 1940s and 1950s there was a major expansion of global Al production utilising the Hall-Héroult process and as a result there were several examples of serious F pollution in the vicinity of Al smelters. In Norway large areas of pine forest were destroyed and grazing animals were affected (Robak, 1969; Arnesen et al., 1995), in Ontario, Canada, cattle suffered from severe fluorosis (Krook and Maylin, 1979), in Scotland, UK, farm animals suffered from severe fluorosis (Gilbert, 1985) and in N. Wales, UK, Walton (1985, 1987) recorded concentrations of up to 8500 mg kg⁻¹ F in bones and damage to teeth of small rodents. As a result of the early problems associated with Al smelting the industry adopted clean technologies using scrubbing systems etc, resulting in a dramatic decrease in F emissions (Ouellet, 1987; Vike and Håbjørg, 1995; Preunkert and Legrand, 2001). Cape et al. (2003) suggested that emissions of F had fallen by a factor of 100 in the previous 50 years. Subsequently, F emissions have been reduced even further and it has been estimated that modern Al smelters produce 15 – 30 kg of F per tonne of Al produced but scrubbing reduces this to < 300 g per tonne (Tjahyono et al., 2011).

However, environmental problems related to F release from Al smelters still occur. Rodriguez et al. (2012) determined the concentrations of F deposited on deciduous tree leaves around an Al smelter in Puerto Madryn, Patagonia. The highest value recorded was over 3650 mg kg⁻¹ with analysis of several species revealing that there was a distance decline in F concentrations from the smelter to 6 km away. Talovskaya et al. (2015) report F concentrations in snow melt water around the Al smelters at Bratsk, Krasnovarsk and Sayanogorsk in SW Siberia. Concentrations of F in the melt water were 37 mg kg⁻¹ at 0.5 km from the Sayanogorsk smelter, 18 mg kg⁻¹ at 3 km from the Bratsk smelter and 12 mg kg⁻¹ at 1 km from the Krasnovarsk smelter. In all cases there was pronounced distance decline in F contents of snow melt and in the case of the Sayanogorsk and Krasnovarsk smelters, values of 0.5 to 1 mg kg⁻¹ were recorded at 29-30 km distance. In Victoria, Australia, in the vicinity of the Portland Al smelter, dental and skeletal fluorosis have been identified in kangaroos (Hufschmidt, et al., 2011; Kierdorf et al., 2016). The Portland smelter is recorded as having emitted just under 110 t of F-containing compounds during the period July 2013 – June 2014 (Kierdorf et al., 2016).

The world production of primary Al in 2017 was 63 Mt (World Aluminium, 2018). According to Tjahyono et al. (2011), most large Al smelters limit F emissions to 0.5-0.6 kg F/t Al. This should have resulted in the release of between 32,000 and 38,000 t of F, however, on the basis of the F emission intensity (kg F/ t Al) of 0.64 for 2017 quoted by World Aluminium (2018) the amount of F released would have been 41,000 t. This is somewhat higher than previous estimates (Jayarathne et al., 2014).

5.4. Phosphoric acid and phosphate fertiliser manufacture

Phosphoric acid is manufactured from phosphate rock, which is essentially composed of apatite. Two methods are utilised for the production of phosphoric acid, a wet process and a thermal process (Weinstein and Davison, 2004; Villalba et al., 2008). In the wet manufacturing process the phosphate rocks are reacted with acid, which can be hydrochloric, nitric or sulfuric acid, however, for the manufacture of fertilisers sulfuric acid is used. The thermal process involves conversion of the phosphate rock to elemental phosphorus which is subsequently converted to phosphoric acid. The production of fertilisers utilises 88% of the phosphate rock extracted globally (UN Food and Agriculture Organisation, 2017) and the wet method of phosphoric acid production for fertiliser manufacture accounts for about 90% of global phosphoric acid production (Tayibi et al., 2009).

Phosphate rock, which is extracted from several countries, contains appreciable quantities of F with those being utilised for fertiliser production generally containing from 2-4% F (EFMA, 2000). During the wet process much of the F is converted to HF and SiF₄ (Weinstein and Davison, 2004) with 10-15% of these compounds being volatilised (EFMA, 2000). In addition, for every tonne of H₃PO₄ produced, about 5 to 5.4 t of waste phosphogypsum (mainly CaSO₄) are also produced, this being stored in ponds (EFMA, 2000; Villalba et al., 2008). This waste product also contains F with Tayibi et al. (2009) listing values of 0.15 – 1.20 wt % F in phosphogypsum from world sources. The phosphogypsum pond waters also typically contain 4-14 g L⁻¹ F (Weinstein and Davison, 2004). In the thermal process much less F is released, with some SiF₄ produced during the initial conversion of the phosphate rock to phosphorus (Villalba et al., 2008).

The volatilisation of F-containing compounds during the wet process has in the past been deemed responsible for serious environmental damage such as the destruction of forest areas in Brazil (Klumpp et al., 1996). Most modern plants have efficient scrubbing systems which according to EFMA (2000) are capable of removing more than 99% of the F-containing compounds. However, it is apparent that even in modern plants there is significant evolution of F-containing compounds. Mirlean and Roisenberg (2007) in a study of F⁻ distribution around a phosphate fertiliser plant in Rio Grande Brazil reported F⁻ values in rainwater of up to 3.04 mg L⁻¹ within 2 km of the plant, the rainwater also having a pH of 4.1. Groundwater near the plant had a correspondingly low pH of 4.1 and elevated F⁻ content of 4.79 mg L⁻¹. The fine fractions of soils (<63 µm) in the vicinity of the plant were found to contain up to 2.37 wt % F. While the source of the F and the acidity in the waters was thought to reflect HF release, the concentrations in soil were thought to be due to appreciable particulate deposition, their F⁻ contents being similar to those in the fertilisers produced. In the vicinity

of a phosphate fertiliser plant in Tunisia, Mezghani et al. (2005) identified chlorosis and necrosis in plants; the plants were found to contain significantly greater F than those of background samples (up to 4x), with F content showing a distance decline over 16 km. This corresponded with measurements of atmospheric F contents. Kierdorf et al. (2016) report that the phosphate fertiliser plant in Portland, Victoria, Australia emitted 17 to 35 t of F⁻ compounds a year between 2002/2003 and 2013/2014.

In addition to the release of F-containing compounds during the manufacture of phosphoric acid, it is apparent that significant quantities are also released from the waste phosphogypsum piles and from the associated water (Weinstein and Davison, 2004; Villalba et al., 2008). Arocena et al. (1995) demonstrated that in phosphogypsum F is strongly enriched in the finest fractions (from 2.5 to 5.7 x) so making it more susceptible to leaching and transport. Dartan et al. (2017) found elevated F⁻ in soils, up to 884 mg kg⁻¹, in the region of fertiliser production units in Turkey. The authors concluded that the source of the F⁻ was mainly from atmospheric transportation from the phosphogypsum piles.

It is apparent that F contamination can also occur as a result of extraction of phosphate rock. Tanouayi et al. (2016) report that dental fluorosis is endemic in the phosphorite mining region of Hahotoe–Kpogame, Togo. The authors concluded that F⁻ pollution of waters, soils and vegetables grown in the region, as a result of the mining, is responsible for the fluorosis problems.

According to the U.S. Geological Survey (2018), global extraction of phosphate rock was 263 Mt in 2017; 88% of all phosphate rock extracted globally is converted to phosphate fertiliser, mostly by the wet process (UN Food and Agriculture Organisation, 2017). Assuming that the mean F content of the phosphate rock is 3 wt % (most sedimentary phosphate rocks, the major occurrence, contain > 3%) and that 10-15% of this is volatilised during production (EFMA, 2000) then in the region of 0.694 – 1.04 Mt of F⁻ would be expected to be released. EFMA (2000) claim that modern phosphate fertiliser plants would scrub out 99% of these releases which would suggest that from 6,900 – 10,400 t of F⁻ would be released annually from phosphate fertiliser production, assuming all plants have efficient scrubbing systems. However, this would be the amount released as gas during the acidification process and would not include any particulates or any subsequent releases from the phosphogypsum. A previous estimate of gaseous and particulate F release during phosphate fertiliser production of 28,000 t is listed in Jayarthne et al. (2014).

5.5. Previous mineral extraction

It has been demonstrated that in the UK, soils in the vicinity of past mining activity where fluorite mineralisation occurs are seriously impacted by F contamination. Fuge and Andrews (1988) quote values for soils in areas adjacent to fluorite-containing mine waste piles in the N. Pennine region of up to almost 2 wt % F and in NE Wales up to 3,500 mg kg⁻¹ F. Andrews et al. (1989) also recorded concentrations of 1wt % F in soils over tailings in the Pennine region with 300 – 1000 mg kg⁻¹ F in vegetation; these authors also note the occurrence of dental fluorosis in field voles in the area. Cooke et al. (1976) report F values of up to 3.8 wt % in tailings in the Derbyshire Peak District with vegetation on the tips containing up to 1 wt

% F, these being some of the highest values recorded in plants (Weinstein and Davison, 2004). More recently Geeson et al. (1998) recorded soil F concentrations of up to 8 wt % in agricultural soils in the Peak District of Derbyshire with Othoo and Abrahams (2016) reporting elevated F in the bones of grazing animals in that region.

China-clay extraction in the St Austell area, Cornwall, has also resulted in F contamination of the local environment. The fine tip material contains up to 1.47 wt % F, soils in the vicinity of the tips contain up to 3,300 mg kg⁻¹ F and unwashed grasses up to 3,240 mg kg⁻¹ F, while the main river draining the area contains 0.44 – 1.25 mg L⁻¹ (Fuge and Andrews, 1988).

5.6. Other industrial sources

Several other sources of environmental F from industrial sources have been mentioned in the literature. Fluorite is used as a flux in the manufacture of steel. Villalba et al. (2007) stated that 1.95 Mt of fluorite was used in the global steelmaking industry in 2003, with over 75% of this consumption being in the developing world. During the steelmaking process HF and SiF₄ are emitted (Semrau, 1957), while it seems that much of the F is retained in the residual slag with Yang et al. (2014) quoting values of 0.44 – 3.37 wt % F (mean 2.02%) in slag from a Swedish steel plant. While there have been instances of serious environmental problems linked to release of F from steelmaking plants, such as the occurrence of fluorosis in farm animals in northern England (Burns and Allcroft, 1964), Weinstein and Davidson (2004) suggest that minor amounts of HF are released to the atmosphere during steelmaking, quoting a value of 104 t a⁻¹.

The use of F-containing materials in the glass and fibreglass, and enamel industries has also resulted in environmental contamination, with HF being emitted (Semrau, 1957). It has been suggested that as much as 20% of the F involved is volatilised in the glassmaking process (Semrau, 1957) with high concentrations of F recorded in some plants in the neighbourhood of glassmaking and enamel factories (Koritnig, 1972). However, Weinstein and Davidson (2004) point out that in developed countries there are now very efficient scrubbing systems in place in glassmaking factories and these have ceased being important sources of environmental F. In addition, data in Villalba et al. (2007), point to the limited amount of fluorite used in the glass and enamel industries relative to that used in the steel industry (<3%). It would seem, therefore, that current emissions from the glassmaking industry are of only limited concern.

There are several industries in which HF is used such as in the manufacture of fluorocarbons and the many other F-containing products. It is essential in the manufacture of semiconductors with Weinstein and Davidson (2004) stating that about 32 t a⁻¹ of HF were released by the semiconductor industry into the USA environment during the 1990s.

Hydrofluoric acid is used in the petroleum industry as a catalyst in the upgrading of light alkenes, such as butene and propene, to produce alkylates, which are important additives in high octane fuels. About 2 kg of HF are used per m³ of alkylate (Villalba et al., 2007).

Lewandowska et al. (2013) suggest that F is emitted from motor vehicle exhaust as a result of its incorporation into fuels, citing it as a source of F in aerosols in urban areas on the Baltic coast of Poland.

6. Agricultural sources of fluorine in the environment

6.1. Application of phosphate fertiliser

As outlined in section 5.4., phosphate fertiliser is manufactured from phosphate rock, which generally contains 2-4 wt % F (EFMA, 2000). During the process some of the F is lost to volatilisation and some is transferred to the waste phosphogypsum. However, it is apparent that appreciable quantities of F are retained in the fertiliser (Table 5). In addition, Cronin et al. (2000) suggest that HF gas scrubbed out of the effluent gases is frequently added back into the fertiliser during subsequent processing, so increasing the F content of the final product. In a study of phosphate fertilisers used in India, Ramteke et al. (2018) found that between 3.14 and 74.8 % of the original F remains in the fertiliser.

Loganathan et al. (2007) calculated that single superphosphate fertiliser applications to soil in New Zealand amounting to 10-30 kg of P ha⁻¹ a⁻¹ added between 1 and 6 kg F ha⁻¹ a⁻¹.

Ramteke et al. (2018) suggested that during 2011-2012, 10.2 Mt of single superphosphate fertilizer was applied to soils in India along with 4.79 Mt of diammonium phosphate. Using these figures Ramteke et al. (2018) calculated that 128,000 ± 14,550 t a⁻¹ of F⁻ were added to soil in India.

As F⁻ is strongly retained in most agricultural soils due to its adsorption by clay minerals and Al- and Fe- oxyhydroxides etc, where phosphate fertiliser has been applied over several years it has been shown that there is a build-up of soil F. Loganathan et al. (2003) and Hedley et al. (2007) carried out studies of soils in New Zealand with a history of prolonged periods of phosphate fertiliser application. Comparison of sites with similar soil types where there had been no phosphate fertiliser applications to those where phosphate fertiliser had been applied over several years showed marked increases of F content, such as 116 to 259 mg kg⁻¹, after application of 765 kg P ha⁻¹ over 20 years as single superphosphate, and 133 to 226 mg kg⁻¹, after application of 60 kg P ha⁻¹ a⁻¹ for 10 years as single superphosphate. However, a more recent study of a trial site in Ireland, where 930 kg P ha⁻¹ had been applied over 31 years as triple superphosphate, demonstrated that while the content of F in the soil had increased by 60 kg ha⁻¹, the increase was statistically insignificant (McGrath and Tunney, 2010).

As F⁻ added to soil during phosphate fertiliser application is generally strongly bound it is not taken up by vegetation and so there is limited intake of F from herbage into grazing animals. However, Loganathan et al. (2007) suggest that much of the added F tends to remain in surface soils, thus, ingestion of the fertilised soils represents a pathway for F into grazing animals (Cronin et al. 2000). Hedley et al. (2007) state that F intake to livestock is mainly from soil ingestion and that a build-up of F in soils following long term application of phosphate fertilisers poses a potential risk of fluorosis.

In 2017 global extraction of phosphate rock was 263 Mt (U.S. Geological Survey, 2018) and 88% of this was converted to phosphate fertiliser (UN Food and Agriculture Organisation, 2017). Literature data for the F⁻ content of phosphate fertilisers suggests that it ranges widely between 0.14 and 3.8 wt % (Table 5). Assuming phosphate fertilisers contain an average of 1wt % F⁻ then at least 2.3 Mt of F⁻ are added to agricultural soils annually, which make it the largest source of anthropogenically-derived F. However, the fertiliser-derived F is strongly

held in soil and is essentially bio-unavailable to plants but could pose a threat to grazing animals due to soil ingestion (Cronin et al., 2000; Hedley et al., 2007).

In addition to the problems of fertiliser F with regard to grazing animals there is also a problem of potential contamination of groundwater. Loganathan et al. (2007) suggest that in more acidic soils F^- can migrate down the soil profile and into shallow groundwater. However, it seems more likely that such a migration of F^- will occur under more alkaline conditions (Pickering, 1985). Groundwater contamination with F^- deriving from phosphate fertiliser has been suggested to occur in West Bengal, India and in the Punjab, Pakistan. In West Bengal, Kundu and Mandal (2009) found that elevated F^- in groundwater was positively correlated with the amount of single superphosphate fertilizer applied to soils in the area. In Punjab, Farooqi et al. (2009) recorded concentrations of up to 22.8 mg L^{-1} F^- in groundwater that the authors claimed derived from F^- which had accumulated in soils due to phosphate fertiliser application. It was suggested in the case of the Punjab that F^- had been mobilised due to the high alkalinity of the soils resulting from the use of fertilisers.

6.2. Other agricultural sources

Application of sewage sludge to agricultural land is widely practised and is a major source of disposal. Davis (1980) showed that application of sewage sludge containing $33,000 \text{ mg kg}^{-1}$ F to pasture in an area of the UK resulted in fluorosis in cattle, possibly linked to excessive uptake of F in ryegrass and/or due to soil ingestion. The excessive F content of the sludge in question was due to an influx of F into the sewage system from an industrial source. In view of the present day regulation of industrial outfalls such extreme F concentrations in sewage sludge are less likely. According to Kabata-Pendias and Pendias (2001) sewage sludge would normally be expected to contain from $2\text{--}740 \text{ mg kg}^{-1}$, with the US EPA (1985) quoting a mean value of 86 mg kg^{-1} and a 95th percentile of 739 mg kg^{-1} for sewage sludge in the USA.

Fluorine in sewage sludge is likely to derive from many sources. In addition to natural sources such as weathering of rocks and leaching from soil together with wind-blown dust, there are many anthropogenic sources. Fluoride is added to potable water in some areas to aid dental health, similarly it is added to toothpaste and mouthwashes. In addition, many pharmaceuticals contain F, along with herbicides and insecticides etc. The F content of sewage sludge added to agricultural land is subject to limitation, e.g. 200 mg kg^{-1} in the UK (Department for Environment, Food & Rural Affairs and Environment Agency, 2018), and is, therefore, likely to add considerably less F to soils than phosphate fertiliser. However, it seems from Davis (1980) that F added to soil in sewage sludge is considerably more bioavailable than that from phosphate fertiliser.

A large number of organofluorine agrochemicals are in common use as insecticides, fungicides, herbicides, acaricides and nematicides (Jescke, 2010) with most being aromatic compounds (Weinstein and Davison, 2004). Most of these agrochemicals are polyfluorinated and are not subject to de-fluorination and undergo only limited biodegradation (Key et al., 1997) so it seems likely that they remain in soil or are transferred to surface or groundwater.

Groundwater in many parts of the world is enriched in F^- (Edmunds and Smedley, 2013; Ali et al., 2016) and some of these waters are used for irrigation of agricultural land. Scholz et al. (2015) found that experimental irrigation of plants with water containing 3 or 5 mg L^{-1} resulted in little root uptake but there were significant increases of foliar F due to overhead irrigation. The use of F-rich waters to irrigate agricultural land was suggested by Botha et al. (1993) to be, in part, responsible for the occurrence of fluorosis in farm animals in a region of South Africa.

7. Anthropogenic sources of fluorine in the urban environment

Many of the sources of environmental F discussed in the earlier sections can seriously impact urban environments, for example when F-emitting industries are sited in the peri-urban environment. In several cities in SE Asia artisanal brick-making results in major F emissions which impact the urban environment (Schmidt, 2013). In SW Siberia the Krasnovarsk aluminium smelter impacts the city of the same name. Coal combustion within homes in China has resulted in fluorosis, while Lewandowska et al. (2013) suggested that one source of elevated F contents of aerosols in urban areas on the Baltic coast of Poland was burning of coals for domestic heating. Lewandowska et al. (2013) also highlighted the role of motor vehicles in F pollution of urban aerosols which they suggested were derived from inclusion of F in high octane fuels and from teflon seals used in the construction of the vehicles.

As a result of the many uses of F in modern society, significant quantities of F-containing materials occur in municipal solid waste (MSW). During incineration of MSW much of the F is released as HF with amounts of up to 20 mg Nm^3 (m^3 at STP) occurring in the gas emitted, this being reduced to 0.01 – 0.1 mg Nm^3 after treatment (Quina et al., 2011). Emissions of HF from incinerators are strictly controlled with a maximum admissible content of 1 mg Nm^3 (Quina et al., 2011). Weinstein and Davidson (2004) indicate that combustion of fluoropolymers would not only release HF but would also release organofluorine compounds including trifluoroacetic acid (TFA). It is worth noting that while modern incinerators are subject to stringent emission standards, uncontrolled burning of refuse and bonfires in gardens and backyards could represent a significant local source of HF and organofluorine compounds in urban environments.

8. Fluorinated organic compounds in the environment

A large number of fluorinated organic compounds occur in the environment and while about 30 of these occur naturally, the vast majority are of anthropogenic origin (Weinstein and Davidson, 2004). Most naturally occurring organofluorine compounds derive from biological sources (Key et al., 1997) but some have been identified in volcanic and geothermal gases and within minerals such as fluorite (Gribble, 2002). Key et al. (1997) point out that all known biologically-derived organofluorine compounds contain only one atom of F while in contrast many human-made fluorocarbons contain multiple F atoms, with over a million containing the trifluoromethyl group (CF_3) (Solomon et al., 2016). The C-F bond is the strongest in nature (Key et al., 1997) and while organofluorine compounds containing one or two F atoms are generally de-fluorinated in the environment, those that contain multiple F

atoms are not de-fluorinated and undergo limited degradation (Key et al., 1997; Solomon et al., 2016).

Manufactured organofluorine compounds have a wide range of uses, from agricultural and pharmaceutical products through to the fluoropolymers used in the manufacture of many items. The major concern is with compounds where all of the H atoms in the C-H bonds are replaced by F, the perfluorinated compounds (PFCs), particularly those with long chains, with 6 or more carbons (Solomon et al., 2016). PFCs are water and grease repellents and have been widely used as stain resistant sprays, for carpets and upholstery for instance, in water-proof clothing, cleaning products, latex paint and fire retarding foams (Calafat et al., 2007; Stahl et al., 2011). PFCs have been widely used in food packaging with a recent study of fast food packaging in the USA detecting them in 20 – 56% of the various packaging materials (Schaidler et al., 2017). PFCs are persistent in the environment and have found their way into the biosphere, where they have been found to bioaccumulate and biomagnify (Houde et al., 2006), and humans where they can bioaccumulate in the brain, liver, lung, bone and kidney (Perez et al., 2013). It has been estimated that 98% of the USA population have detectable PFCs in blood (Kataria et al., 2015). The major pathways into humans are via diet, with fish, shellfish and potatoes being major contributors (Ji et al., 2012), together with drinking water and inhalation of indoor air (Stahl et al., 2011).

PFCs have been linked to several human health problems including cancers, thyroid disease and immunotoxicity (Schaidler et al., 2017) and have been shown to affect the renal system (Kataria et al., 2015). In addition, PFCs can cross the placental barrier into the foetus (Yang et al., 2016) with this being linked to reduced foetal growth (Callan et al., 2016). Some of the long chain PFCs are now listed as persistent organic pollutants (POPs) and in some cases their manufacture has been banned.

The most well-known and notorious fluorocarbon compounds are the chlorofluorocarbons or CFCs. They were introduced in the mid-1900s in refrigeration and air conditioning systems, in fire extinguishers and as propellants in aerosol cans etc. In the 1970s it was realised that the CFCs were causing serious ozone depletion. Their production was limited in the 1990s and they are being totally phased out (McCulloch, 2003). The CFCs have essentially been replaced with hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs) that do not result in ozone depletion (Weinstein and Davidson, 2004).

In addition to being involved in ozone depletion, the CFCs along with HFCs and HCFCs are serious greenhouse gases and together with other F-containing gases such as SF₆ and NF₃ represent 2% of global greenhouse gas emissions (IPCC, 2014). According to the US EPA (2018) in 2016, 92% of the F-containing greenhouse gases derived from the CFC substitutes with small amounts deriving from such sources as aluminium production and semiconductor manufacture. The F-containing greenhouse gases have long atmospheric lifetimes ranging up to several thousand years (US EPA, 2018).

Degradation of some of the CF₃-containing compounds released into the environment such as the HFCs and the HCFCs will result in the formation of trifluoroacetic acid (TFA – CF₃COOH) (Bouttonnet et al., 1999). In addition some TFA is released to the environment

through its manufacture (Key et al., 1997), from pyrolysis of fluoropolymers (McCulloch, 2003) and the burning of household waste (Weinstein and Davidson, 2004). TFA is stable in the environment (Boutonnet et al., 1999) and rapidly forms acetate salts such as CF_3COONa (Solomon et al., 2016). TFA, mainly in the form of its salts, occurs in air, soils, precipitation and surface water but its concentration in these media shows large geographic variations; while its concentration is low in remote areas of the world (Boutonnet et al., 1999), it is elevated in the atmosphere and rainfall of urban and industrial areas (Weinstein and Davidson, 2004). It tends not to be retained in soils and is probably carried into groundwater (Solomon et al., 2016). According to Solomon et al. (2016) TFA accumulates in playas, salt-lakes and the sea due to evapoconcentration, however, its concentration in seawater is considerably greater than would be expected from accumulation through the recent past, suggesting an additional natural source. Seawater in close proximity to hydrothermal vents in the seabed has been found to be enriched in TFA and such hydrothermal outputs have been suggested to be a source of its natural enrichment in seawater (Solomon et al., 2016).

De Angelis and Legrande (1994) suggest that increased F^- contents of Greenland snow in the late 1900s are, in part, a result of CFC degradation, while Preunkert and Legrande (2001) state that degradation of HCFCs may have contributed to the F^- budget of Alpine snow during 1980 – 1995.

9. Conclusions

Fluorine in the environment mainly derives from weathering of the lithosphere, its major reservoir in the lithosphere being OH-containing minerals where F^- substitutes for OH^- . Of the other natural sources of environmental F, volcanicity is the most important but wind-blown dust and biomass burning make significant contributions. While it has been suggested that marine-derived F is a major source to the environment it seems likely that its contribution has been over estimated and that it constitutes only a minor fraction of the total additions.

While concentrations of up to 8 wt % F have been recorded in soils of fluorite mineralised areas of the UK with up to 1wt % F recorded in plants, the most significant anthropogenic source of environmental F is the addition of phosphate fertiliser to agricultural soils, which is estimated to add at least 2.3 Mt annually. While much of this is strongly held in soil, it is possible that some of the F will be mobilised into groundwater. Of the other anthropogenic sources coal combustion has been widely held to be the major contributor. However, it seems likely that at present brickmaking is the major anthropogenic source of F. The rapid growth of urban areas in India, Pakistan and Bangladesh has seen a corresponding growth of brickmaking in these countries and together with China they are responsible for over 75% of global brick production. As many of the brick kilns in operation in these countries are artisanal and unregulated they represent a serious source of HF emissions. Using data from the literature it is possible to estimate that global brick production releases about 1.8 Mt a^{-1} F. From data in Table 6 it can be estimated that total gaseous emissions of F from anthropogenic sources are in the order of 2.2 Mt a^{-1} , suggesting that F emissions from brickmaking far

outweigh those of coal combustion, Al smelting and the manufacture of phosphate fertilisers, and even the major natural source of vulcanicity.

Studies on ice cores from Greenland and from the French and Swiss Alps reveal that their contained F is derived from relatively local sources (De Angelis and Legrand, 1994; Preunkert and Legrand, 2001). Therefore, it seems likely that while atmospheric F emissions represent a major threat to local environments, they are not transported globally. Within the urban environment, the occurrence of industrial sources of F emission in the periurban environment can have an impact, while domestic coal combustion and the release of F from high octane fuels in motor vehicles are also potential sources.

Fluorine has a wide range of uses in modern society it being incorporated into many compounds used in medicine and agriculture, and in the many fluoropolymers currently manufactured. Degradation of some of these fluorocarbon compounds, along with pyrolysis of fluoropolymers and the burning of household refuse containing them has resulted in the recent deposition of organofluorine compounds in the environment.

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Table 1. Fluorine abundances in crustal rocks from literature compilations (mg kg⁻¹)

Rock type	1	2	3
Ultramafic rocks		50 – 100	20
Basalts & gabbros	400	300 – 500	300
Intermediate rocks	500	500 – 1200	
Granites	735	520 – 850	800
Rhyolites		300 – 700	
Shales	740	500 – 800	700
Sandstones	270	50 – 270	200
Carbonates	330	50 – 350	300

1. Levinson (1980); 2. Kabata-Pendias and Pendias (2001);
3. Reimann and Caritat (1998)

Table 2. Fluorine-rich rocks (mg kg⁻¹)

Rock type	Range	Mean (no.)	Ref
Greisenised granite, Germany		20,400 (24)	1
Greisenised granite, SW England, UK	8,040 – 27,700	15,500 (5)	2
Granite pegmatites, SW England, UK	365 – 22,700	7,550 (14)	2
Fluorite granite, St. Austell, SW England, UK	1,070 – 10,400	4,380 (11)	2
Granite, central Colorado, USA	70 – 260,000	1,100 (459)	3
Phonolites/trachytes/nephelinites, Eastern rift	1000 – 4,900	2,500 (27)	4
Carbonatites, Africa	216 – 25,200	6,500 (12)	5
Sedimentary phosphorites, global	37,000 – 40,000	38,500 (4)	6

1. Koritnig (1972); 2. Fuge and Andrews (1988); 3. Wallace (2010); 4. Hayes et al. (2017);
5. Dawson and Fuge (1980); 6. EFMA (2000)

Table 3. Fluorine in soils (mg kg⁻¹)

Source	Range	Mean (no.)	Ref
World		200	1
World		400 (median)	2
Former USSR	30 – 320	200	3
USA	<10 – 3700	430	4
UK	113 – 580	350 (144)	5
New Zealand	212 – 617	357	6
World - podzols	<10 – 1,100	130	7
World - cambisols	<10 – 800	385	7
World - rendzinas	<10 – 840	360	7
World – kastanozems & chernozems	10 – 1,194	550	7
World - histosols	10 – 335	220	7
Sn/W mineralised area, SW England	1,335 – 5,250	2410 (54)	5
Fluorite mineralised area, Colorado	40 – 7160	630 (209)	8
F-rich granites, SW England	370 – 12,600	1930 (178)	9

1. Levinson (1980); 2. Reimann and Caritat (1998); 3. Vinogradov (1967);
4. Shacklette and Boerngen (1984); 5. Fuge and Andrews (1988);
6. Loganathan et al. (2006). 7. Kabata-Pendias and Pendias (2001); 8. Wallace (2010);
9. Fuge (unpublished data)

Table 4. Comparison of fluorine content of brick-making clays before and after roasting (mg kg⁻¹)

Material	Range	Mean
Chinese soils – clay-rich ¹	295 – 800	490
Chinese soils after roasting at 1100 °C ¹	53 – 112	74
Marine deposited clays, UK ²	501 – 993	807
Marine clays, UK, after roasting at 1000 °C ²	70 – 332	154
Non-marine deposited clays, UK ²	263 – 572	390
Non-marine clays, UK, after roasting at 1000 °C ²	<50 – 237	75

1. Data from Xie et al. (2003)
2. Data from Fuge and Hennah (1989)

Table 5. Fluorine in phosphate fertiliser (%)

Material	Range	Mean	Ref.
Phosphate fertiliser, global	0.85 – 3.80		1
Single superphosphate, New Zealand	1.08 – 1.84		2
Triple superphosphate, New Zealand	1.30 – 2.40		2
Monoammonium phosphate, New Zealand	1.60 – 2.20		2
Diammonium phosphate, New Zealand	1.20 – 3.00		2
Single superphosphate, India	0.42 – 1.16	0.86 (4)	3
Diammonium phosphate, India	0.14, 1.07	0.61 (2)	3
Ammonium nitrophosphate, India		1.33	3

1. Kabata-Pendias and Pendias (2001); 2. Cronin et al. (2000);
3. Ramteke et al. (2018)

Table 6. Major sources of fluorine in the environment

Source	Estimate MMT a ⁻¹	Ref
Vulcanicity	0.3 – 0.7	1
Biomass burning	0.076	2
Coal combustion	0.2 – 0.3	3
Brickmaking	1.8	3
Al smelting	0.41	3
Manufacture of phosphate fertiliser	0.07 – 0.10*	3
Application of phosphate fertiliser	2.3	3

*Amount released in gas. Total including F released in particulates and from phosphogypsum is much higher – Jayarathne et al. (2014) quote a total value of 0.28 MMT a⁻¹.

1. Based on data in Pyle and Mather (2009)
2. Jayarathne et al. (2014);
3. Current paper